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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵ : C08F 4/76, 4/603, 10/00	A1	(11) International Publication Number: WO 91/09882 (43) International Publication Date: 11 July 1991 (11.07.91)
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(54) Title: SUPPORTED IONIC METALLOCENE CATALYSTS FOR OLEFIN POLYMERIZATION (57) Abstract A supported catalyst for olefin polymerization comprising a Group IV-B metallocene component and an ionic activator component comprising a cation capable of donating a proton and a labile bulky anion having a plurality of lipophilic radicals so that the anion is sterically hindered from covalently bonding with a cation produced from the Group IV-B metal of the metallocene.		

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SUPPORTED IONIC METALLOCENE CATALYSTS
FOR OLEFIN POLYMERIZATION

Background of the Invention

1. Field of the Invention

1 The invention relates to supported catalysts for
2 polymerization of olefins including gas or slurry phase
3 polymerization of olefins, diolefins, cyclic olefins and
4 acetylenically unsaturated monomers. These catalysts, which may be
5 supported on known catalyst supports, include a Group IV-B metal
6 metallocene compound and an ionic activator compound. While the
7 homogeneous variant of this catalyst system has been previously
8 disclosed in copending U.S. Serial No. 133,480, a supported form of
9 the catalyst system has not heretofore been produced. The supported
10 catalyst, suitable for use in gas or slurry phase olefin
11 polymerization, provides a polymer product having a narrower particle
12 size distribution and higher bulk density than achievable with the
13 homogeneous catalyst system. Furthermore, the use of the supported

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1 catalyst in the gas phase results in greatly reduced reactor fouling
2 as compared to the unsupported or homogeneous variant. By employing
3 suitably sized supports, the catalyst system can be employed in
4 solution and high pressure polymerization processes.

5

2. Background

6 Ziegler-Natta type catalysts for the polymerization of
7 olefins are well known. The traditional Ziegler-Natta type systems
8 comprise a metal halide activated to a catalyst species by reaction
9 with a metal alkyl cocatalyst, particularly an aluminum alkyl
10 cocatalyst. The activation of these traditional Ziegler-Natta
11 catalysts generates a variety of different active sites. As a
12 consequence of this non-uniformity of the active sites, the catalysts
13 produce polymer products of broad molecular weight distribution
14 (MWD). Furthermore, the copolymer products exhibit broad composition
15 distribution (CD), poor comonomer incorporation and blocky sequence
16 distribution.

17 Recently it has been found that active catalysts are formed
18 when a bis(cyclopentadienyl) compound of the Group IV-B metals, in
19 particular zirconium and hafnium, is activated by an alumoxane. The
20 metallocene-alumoxane catalysts whether homogeneous or supported
21 generally possess high activity and are more versatile than
22 conventional Ziegler-Natta catalysts in that they may be effectively
23 used to produce a variety of polymer products including, for example,
24 high density linear polyethylene (HDPE), linear low density
25 polyethylene (LLDPE), ethylene-propylene copolymer (EP),
26 non-crystalline polypropylene and crystalline polypropylene. The
27 metallocene-alumoxane catalysts also offer the significant advantage
28 over the traditional Ziegler-Natta catalysts of being able to produce
29 polymers with narrow MWD.

30 While the metallocene-alumoxane catalysts do offer
31 significant advantages over the traditional Ziegler-Natta catalysts,
32 they nevertheless have limitations in practical commercial
33 applications. These limitations include the relatively high cost of
34 the alumoxane cocatalysts. Alumoxane is also air sensitive and

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1 difficult to manipulate. Furthermore, the metallocene-alumoxane
2 catalysts, while producing a narrow MWD polymer product, have a
3 limited capability to produce high molecular weight polymers or
4 polymers having a high comonomer content.

5 Copending U.S. Patent Application Serial No. 133,480, also
6 published as European Patent Application 277,004 which is hereby
7 incorporated by reference, describes a further advance in metallocene
8 catalysts: a new metallocene catalyst which does not require either
9 an alkyl aluminum or an alumoxane as an activator. The Group IV-B
10 metallocene catalyst is prepared as a reaction product of a Group
11 IV-B metal metallocene compound and an ionic activator compound. The
12 ionic activator comprises a cation having a donatable proton and a
13 labile, bulky anion which is a single coordination complex having a
14 plurality of lipophilic radicals covalently coordinated to and
15 shielding a central charge-bearing metal or metalloid atom, the bulk
16 of said anion being such that upon reaction of the activator cation
17 donatable proton with a proton reactable substituent of a
18 bis(cyclopentadienyl) Group IV-B metal compound to form a Group IV-B
19 metal cation, the anion of the activator is sterically hindered from
20 covalently coordinating to the Group IV-B metal cation. Hence, as
21 described in the copending application, an active catalytic species
22 of a metallocene is formed, namely an ionic pair comprising a
23 metallocene transition metal cation paired with a noncoordinating
24 anion of the activator component.

25 The new metallocene catalyst system (hereafter referred to
26 as an "ionic metallocene catalyst") eliminates the need for an
27 expensive alumoxane activator. The ionic metallocene catalyst also
28 offers other advantages over the metallocene-alumoxane catalysts such
29 as permitting the production of polyolefin products of narrow MWD and
30 of significantly higher weight average molecular weight at high rates
31 of catalytic activity while also permitting better incorporation of
32 comonomers and the control of the chain end chemistry of the polymer

33 The new ionic metallocene catalyst of the copending
34 application is, however, a homogeneous catalyst and generally can not
35 be practically used for gas phase polymerization. The use of a

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1 supported catalyst offers the possibility of gas phase
2 compatibility. Control of the particle size distribution of the
3 polymeric product in the various polymerization processes eliminates
4 or reduces the extent of reactor fouling.

5 Supported catalysts for olefin polymerization are well known
6 in the art. These catalysts offer, among others, the advantages of
7 being usable in gas or slurry phase reactors allowing the control of
8 polymer particle size and thereby the control of product bulk
9 density. Gas phase reactors also eliminate the need for a solvent
10 and the equipment for solvent handling and separation. However, the
11 known Ziegler-Natta olefin polymerization supported catalysts also
12 present disadvantages which include broad MWD and composition
13 distribution (CD), inefficient incorporation of comonomers, poor
14 sequence distribution and, in the case of lower activity catalysts,
15 the need for a product deashing step.

16 Supported metallocene-alumoxane catalysts for olefin
17 polymerization are described in U.S. Patent 4,701,432 of Welborn.
18 These supported metallocene-alumoxane catalysts are obtained by
19 reacting a metallocene and an alumoxane in the presence of the solid
20 support material. The supported catalyst may then be employed either
21 as the sole catalyst component or may be employed in combination with
22 an organometallic cocatalyst. The supported metallocene-alumoxane
23 catalyst, however, still produces polymers of generally lower
24 molecular weight and comonomer incorporation than desired for certain
25 applications.

26 It would be desirable to provide a supported catalyst for
27 gas or slurry phase olefin polymerization that eliminates the need
28 for either an alumoxane or an alkyl aluminum cocatalyst. It would be
29 further desirable that such supported catalyst be capable of
30 providing a polymer product having a high molecular weight, narrow
31 MWD and CD, good comonomer incorporation, good sequence distribution,
32 high bulk density and controlled particle size for ease of removal
33 from the reactor.

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Summary

1 The invention provides a supported ionic metallocene
2 catalyst which is suitable for use in the polymerization of olefins
3 including gas or slurry phase polymerization of olefins. The
4 heterogeneous catalyst, like its homogeneous counterpart disclosed in
5 our European Patent Application EP 277 004, permits the production of
6 polyolefins of high molecular weight and narrow molecular weight
7 distribution (MWD) at high rates. Moreover, the polyolefin products
8 of the supported catalyst have a narrow composition distribution (CD)
9 and improved sequence distribution of comonomers as compared to the
10 products of prior art conventional supported Ziegler-Natta catalysts.

11 The possibility of producing a supported catalyst was
12 surprising since it would have been predicted that the reaction of
13 ionic catalyst as described in the copending application with a Lewis
14 base such as is present on a metal oxide surface would result in
15 catalyst deactivation. This invention is even more surprising since
16 aluminum alkyls are not present during catalyst preparation and
17 furthermore the polymer products are similar to that obtained with
18 the unsupported catalyst.

19 The supported ionic metallocene catalyst of this invention
20 comprises the ionic metallocene catalyst and a suitable support
21 material. The metallocene component of the ionic metallocene
22 catalyst may be selected from a bis(cyclopentadienyl) derivative of a
23 Group IV-B (Periodic Table of Elements, published and copyrighted by
24 CRC Press, Inc., 1984) metal compound containing at least one ligand
25 which will combine with an activator component or at least a portion
26 thereof such as a cation portion thereof. The activator component is
27 an ionic compound comprising a cation which will irreversibly react
28 with at least one ligand contained in said Group IV-B metal compound
29 (metallocene component) and an anion which is a single coordination
30 complex comprising a plurality of lipophilic radicals covalently
31 coordinated to and shielding a central formally charge-bearing metal
32 or metalloid atom, which anion is bulky, labile and stable to any
33 reaction involving the cation of the activator component. The
34 charge-bearing metal or metalloid may be any metal or metalloid

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1 capable of forming a coordination complex which is not hydrolyzed by
2 aqueous solutions. Upon combination of the metallocene component and
3 activator component, the cation of the activator component reacts
4 with one of the ligands of the metallocene component, thereby
5 generating an ion pair consisting of a Group IV-B metal cation with a
6 formal coordination number of 3 and a valence of +4 and the
7 aforementioned anion, which anion is compatible with and
8 noncoordinating toward the metal cation formed from the metallocene
9 component. The anion of the activator compound must be capable of
10 stabilizing the Group IV-B metal cation complex without interfering
11 with the ability of the Group IV-B metal cation or its decomposition
12 product to function as a catalyst and must be sufficiently labile to
13 permit displacement by an olefin, diolefin or an acetylenically
14 unsaturated monomer during polymerization.

15 Either the ionic metallocene catalyst or both its components
16 will be contacted with an inorganic or organic solid support
17 material, either thermally or chemically dehydrated before such
18 contact, to form the supported ionic metallocene catalyst of this
19 invention.

20 The method for preparing these supported ionic catalyst
21 comprises the steps of,

22 (a) combining, in a solvent or diluent

23 (i) at least one metallocene component comprising a
24 bis(cyclopentadienyl) metal compound containing at least one ligand
25 capable of reacting with a proton, said metal being selected from
26 Group IV B metals,

27 (ii) at least one activator component comprising a
28 cation capable of donating a proton and an anion, said anion being a
29 single coordination complex comprising a plurality of lipophilic
30 radicals covalently coordinated to and shielding a central
31 charge-bearing metal or metalloid atom, said anion being bulky,
32 labile and capable of stabilizing the metal cation formed as a result
33 of reaction between the two, and

34 (iii) a catalyst support material suspended in a
35 suitable solvent, and

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1 (b) recovering a supported catalyst product as a
2 free-flowing solid or slurry.

3 The supported catalyst of this invention will polymerize
4 olefins, diolefins and/or acetylenically unsaturated monomers either
5 alone or in combination with other olefins and/or other unsaturated
6 monomers in liquid, slurry or gas phase reactions.

7 In general, catalysts can be selected so as to produce the
8 polymer products which will be free of certain trace elements
9 generally found in polymers produced with Ziegler-Natta type
10 catalysts such as aluminum, magnesium, chloride and the like. The
11 polymer products produced with the catalysts of this invention
12 should, then, have a broader range of applications than polymers
13 produced with either the more conventional Ziegler-Natta type
14 catalysts containing a metal alkyl, such as an aluminum alkyl, or the
15 metallocene-alumoxane catalysts.

16 Detailed Description of the Preferred Embodiments

17 The present invention relates to supported catalysts
18 eminently suited for use in various polymerization processes
19 including gas or slurry phase polymerization of olefins. The
20 heterogeneous catalyst includes a metallocene of the Group IV-B
21 transition metals, an ionic activator compound and a catalyst
22 support. European Patent Application EP 277,004 incorporated by
23 reference, describes the homogeneous variant of the Group IV-B ionic
24 metallocene catalyst which is prepared as the reaction product of a
25 Group IV-B metal metallocene compound and an ionic activator compound.

The Metallocene Component

26 The Group IV-B metal compounds, particularly the titanium,
27 zirconium and hafnium compounds, useful as first compounds in the
28 ionic metallocene catalyst system employed in the process of this
29 invention are the bis(cyclopentadienyl) derivatives of titanium,
30 zirconium or hafnium. In general, such useful titanium, zirconium
31 and hafnium compounds may be represented by the following general
32 formulae:

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- 1 1. $(A-Cp)MX_1X_2$
- 2 2. $(A-Cp)\overline{MX'_1X'_2}$
- 3 3. $(A-Cp)ML$
- 4 4. $(Cp^*)(CpR)\overline{MX_1}$

5 wherein: M is a metal selected from the Group consisting of titanium
6 (Ti), zirconium (Zr) and hafnium (Hf); (A-Cp) is either $(Cp)(Cp^*)$ or
7 $Cp-A'-Cp^*$ and Cp and Cp^* are the same or different substituted or
8 unsubstituted cyclopentadienyl radicals, and wherein A' is a covalent
9 bridging group containing a Group IV-A element; L is an olefin,
10 diolefin or aryne ligand; X_1 and X_2 are, independently,
11 selected from the group consisting of hydride radicals, hydrocarbyl
12 radicals having from 1 to about 20 carbon atoms,
13 substituted-hydrocarbyl radicals, wherein 1 or more of the hydrogen
14 atoms are replaced with a halogen atom, having from 1 to about 20
15 carbon atoms, organo-metalloid radicals comprising a Group IV-A
16 element wherein each of the hydrocarbyl substituents contained in the
17 organo-portion of said organo-metalloid, independently, contain from
18 1 to about 20 carbon atoms and the like; X'_1 and X'_2 are
19 joined and bound to the metal atom to form a metallacycle, in which
20 the metal, X'_1 and X'_2 form a hydrocarbocyclic ring
21 containing from about 3 to about 20 carbon atoms; and R is a
22 substituent, preferably a hydrocarbyl substituent, having from 1 to
23 20 carbon atoms, on one of the cyclopentadienyl radicals which is
24 also bound to the metal atom. Each carbon atom in the
25 cyclopentadienyl radical may be, independently, unsubstituted or
26 substituted with the same or a different radical selected from the
27 Group consisting of hydrocarbyl radicals, substituted-hydrocarbyl
28 radicals wherein one or more hydrogen atoms is replaced by a halogen
29 atom, hydrocarbyl-substituted metalloid radicals wherein the
30 metalloid is selected from Group IV-A of the Periodic Table of the
31 Elements, halogen radicals and the like. Suitable hydrocarbyl and

1 substituted-hydrocarbyl radicals which may be substituted for at
2 least one hydrogen atom in the cyclopentadienyl radical will contain
3 from 1 to about 20 carbon atoms and include straight and branched
4 alkyl radicals, cyclic hydrocarbon radicals, alkyl-substituted cyclic
5 hydrocarbon radicals, aromatic radicals and alkyl-substituted
6 aromatic radicals. Similarly, and when X_1 and/or X_2 is a
7 hydrocarbyl or substituted-hydrocarbyl radical, each may,
8 independently, contain from 1 to about 20 carbon atoms and be a
9 straight or branched alkyl radical, a cyclic hydrocarbyl radical, an
10 alkyl-substituted cyclic hydrocarbyl radical, an aromatic radical or
11 an alkyl-substituted aromatic radical. Suitable organometalloid
12 radicals include mono-, di- and trisubstituted organometalloid
13 radicals of Group IV-A elements wherein each of the hydrocarbyl
14 Groups contain from 1 to about 20 carbon atoms. Suitable
15 organometalloid radicals include trimethylsilyl, triethylsilyl,
16 ethyldimethylsilyl, methyldiethylsilyl, triphenylgermyl,
17 trimethylgermyl and the like.

18 Illustrative, but not limiting examples of
19 bis(cyclopentadienyl)zirconium compounds which may be used in the
20 preparation of the improved
21 (ethylcyclopentadienyl)(cyclopentadienyl) and
22 bis(ethylcyclopentadienyl)zirconium dihydride,
23 (propylcyclopentadienyl)(cyclopentadienyl) and
24 bis(propylcyclopentadienyl)zirconium dihydride,
25 (n-butylcyclopentadienyl)(cyclopentadienyl) and
26 bis(n-butylcyclopentadienyl)zirconium dihydride,
27 (t-butylcyclopentadienyl)(cyclopentadienyl) and
28 bis(t-butylcyclopentadienyl)zirconium dihydride,
29 (cyclohexylmethylcyclopentadienyl)(cyclopentadienyl) and
30 bis(cyclohexylmethylcyclopentadienyl)zirconium dihydride,
31 (benzylcyclopentadienyl)(cyclopentadienyl) and
32 bis(benzylcyclopentadienyl)zirconium dihydride,
33 (diphenylmethylcyclopentadienyl)(cyclopentadienyl) and
34 bis(diphenylmethylcyclopentadienyl)zirconium dihydride and the like;
35 (polyhydrocarbyl-substituted-cyclopentadienyl) zirconium compounds

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1 such as (dimethylcyclopentadienyl) (cyclopentadienyl) and
2 bis(dimethylcyclopentadienyl) zirconium dimethyl,
3 (trimethylcyclopentadienyl) (cyclopentadienyl) and
4 bis(trimethylcyclopentadienyl) zirconium dimethyl,
5 (tetramethylcyclopentadienyl) (cyclopentadienyl) and
6 bis(tetramethylcyclopentadienyl) zirconium dimethyl,
7 (permethylcyclopentadienyl) (cyclopentadienyl) and
8 bis(permethylcyclopentadienyl) zirconium dimethyl,
9 (ethyltetramethylcyclopentadienyl) (cyclopentadienyl) and
10 bis(ethyltetramethylcyclopentadienyl) zirconium dimethyl,
11 (indenyl)(cyclopentadienyl) and bis(indenyl)zirconium dimethyl,
12 (dimethylcyclopentadienyl) (cyclopentadienyl) and
13 bis(dimethylcyclopentadienyl) zirconium dihydride,
14 (trimethylcyclopentadienyl) (cyclopentadienyl) and
15 bis(trimethylcyclopentadienyl) zirconium dihydride,
16 (tetramethylcyclopentadienyl) (cyclopentadienyl) and
17 bis(tetramethylcyclopentadienyl)zirconium dihydride,
18 (permethylcyclopentadienyl) (cyclopentadienyl) and
19 bis(permethylcyclopentadienyl)zirconium dihydride,
20 (ethyltetramethylcyclopentadienyl) (cyclopentadienyl) and
21 bis(ethyltetramethylcyclopentadienyl)zirconium dihydride,
22 (indenyl)(cyclopentadienyl) and bis(indenyl)zirconium dihydride
23 (propylcyclopentadienyl) (cyclopentadienyl) and
24 bis(propylcyclopentadienyl)zirconium dihydride,
25 (n-butylcyclopentadienyl) (cyclopentadienyl) and
26 bis(n-butylcyclopentadienyl)zirconium dihydride,
27 (t-butylcyclopentadienyl) (cyclopentadienyl) and
28 bis(t-butylcyclopentadienyl)zirconium dihydride,
29 (cyclohexylmethylcyclopentadienyl) (cyclopentadienyl) and
30 bis(cyclohexylmethylcyclopentadienyl)zirconium dihydride,
31 (benzylcyclopentadienyl) (cyclopentadienyl) and
32 bis(benzylcyclopentadienyl)zirconium dihydride,
33 (diphenylmethylcyclopentadienyl) (cyclopentadienyl) and
34 bis(diphenylmethylcyclopentadienyl)zirconium dihydride and the like;
35 (metal hydrocarbyl-substituted cyclopentadienyl)zirconium compounds

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1 such as (trimethylsilylcyclopentadienyl)(cyclopentadienyl) and
2 bis(trimethylsilylcyclopentadienyl)zirconium dimethyl,
3 (trimethylgermylcyclopentadienyl)(cyclopentadienyl) and
4 bis(trimethylgermylcyclopentadienyl)zirconium dimethyl,
5 (trimethylstannylcyclopentadienyl)(cyclopentadienyl) and
6 bis(trimethylstannylcyclopentadienyl)zirconium dimethyl,
7 (trimethylplumbylcyclopentadienyl)(cyclopentadienyl) and
8 bis(trimethylplumbylcyclopentadienyl)zirconium dimethyl,
9 (trimethylsilylcyclopentadienyl)(cyclopentadienyl) and
10 bis(trimethylsilylcyclopentadienyl)zirconium dihydride,
11 (trimethylgermylcyclopentadienyl)(cyclopentadienyl) and
12 bis(trimethylgermylcyclopentadienyl)zirconium dihydride,
13 (trimethylstannylcyclopentadienyl)(cyclopentadienyl) and
14 bis(trimethylstannylcyclopentadienyl)zirconium dihydride,
15 (trimethylplumbylcyclopentadienyl)(cyclopentadienyl) and
16 bis(trimethylplumbylcyclopentadienyl)zirconium dihydride and the
17 like; (halogen-substituted-cyclopentadienyl) zirconium compounds such
18 as (trifluoromethylcyclopentadienyl)(cyclopentadienyl) and
19 bis(trifluoromethylcyclopentadienyl)zirconium dimethyl
20 (trifluoromethylcyclopentadienyl)(cyclopentadienyl) and
21 bis(trifluoromethylcyclopentadienyl)zirconium dihydride and the like;
22 silyl-substituted bis(cyclopentadienyl) zirconium compounds such as
23 bis(cyclopentadienyl) (trimethylsilyl)(methyl)zirconium,
24 bis(cyclopentadienyl) (triphenylsilyl)(methyl)zirconium,
25 bis(cyclopentadienyl) [tris(dimethylsilyl)silyl](methyl)zirconium,
26 bis(cyclopentadienyl)[bis(mesityl)silyl](methyl)zirconium,
27 bis(cyclopentadienyl)(trimethylsilyl)trimethylsilylmethyl zirconium,
28 bis(cyclopentadienyl) (trimethylsilylbenzyl) and the like;
29 (bridged-cyclopentadienyl)zirconium compounds such as methylene
30 bis(cyclopentadienyl)zirconium dimethyl; ethylene
31 bis(cyclopentadienyl)zirconium dimethyl, dimethylsilyl
32 bis(cyclopentadienyl)zirconium dimethyl, methylene
33 bis(cyclopentadienyl)zirconium dihydride, ethylene
34 bis(cyclopentadienyl)zirconium dihydride and dimethylsilyl
35 bis(cyclopentadienyl)zirconium dihydride and the like; zirconacycles

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1 such as bis(pentamethylcyclopentadienyl) zirconacyclobutane,
2 bis(pentamethylcyclopentadienyl) zirconacyclopentane,
3 bis(cyclopentadienyl)zirconaindane.
4 1-bis(cyclopentadienyl)zircona-3-dimethylsila-cyclobutane and the
5 like; olefin, diolefin and aryne ligand substituted
6 bis(cyclopentadienyl)zirconium compounds such as
7 bis(cyclopentadienyl) (1,3-butadiene)zirconium, bis(cyclopentadienyl)
8 (2,3-dimethyl-1,3-butadiene)zirconium,
9 bis(pentamethylcyclopentadienyl)(benzyne)zirconium and the like;
10 (hydrocarbyl)(hydride) bis(cyclopentadienyl)zirconium compounds such
11 as bis(pentamethylcyclopentadienyl)zirconium (phenyl)(hydride),
12 bis(pentamethylcyclopentadienyl)zirconium (methyl)(hydride) and the
13 like; and bis(cyclopentadienyl) zirconium compounds in which a
14 substituent on the cyclopentadienyl radical is bound to the metal
15 such as (pentamethylcyclopentadienyl)
16 (tetramethylcyclopentadienylmethylene) zirconium hydride,
17 (pentamethylcyclopentadienyl)
18 (tetramethylcyclopentadienylmethylene)zirconium phenyl and the like.
19 A similar list of illustrative bis(cyclopentadienyl) hafnium
20 and bis(cyclopentadienyl)titanium compounds could be made, but since
21 the lists would be nearly identical to that already presented with
22 respect to bis(cyclopentadienyl)zirconium compounds, such lists are
23 not deemed essential to a complete disclosure. Other
24 bis(cyclopentadienyl)hafnium compounds and other
25 bis(cyclopentadienyl)titanium compounds as well as other
26 bis(cyclopentadienyl)zirconium compounds which are useful in the
27 catalyst compositions of this invention will, of course, be apparent
28 to those skilled in the art.

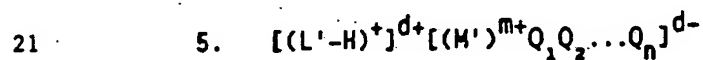
The Activator Component

29 Compounds useful as an activator component in the
30 preparation of the catalyst of this invention will comprise a cation,
31 which is a Bronsted acid capable of donating a proton, and a
32 compatible noncoordinating anion containing a single coordination
33 complex comprising a charge-bearing metal or metalloid core, which

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1 anion is relatively large (bulky), capable of stabilizing the active
 2 catalyst species (the Group IV-B cation) which is formed when the two
 3 compounds are combined and said anion will be sufficiently labile to
 4 be displaced by olefinic, diolefinic and acetylenically unsaturated
 5 substrates or other neutral Lewis bases such as ethers, nitriles and
 6 the like. As indicated above, any metal or metalloid capable of
 7 forming a coordination complex which is stable in water may be used
 8 or contained in the anion of the second compound. Suitable metals,
 9 then, include, but are not limited to, aluminum, gold, platinum and
 10 the like. Suitable metalloids include, but are not limited to,
 11 boron, phosphorus, silicon and the like. Compounds containing anions
 12 which comprise coordination complexes containing a single metal or
 13 metalloid atom are, of course, well known and many, particularly such
 14 compounds containing a single boron atom in the anion portion, are
 15 available commercially. In light of this, salts containing anions
 16 comprising a coordination complex containing a single boron atom are
 17 preferred.

18 In general, the activator compounds useful in the
 19 preparation of the catalysts of this invention may be represented by
 20 the following general formula:



22 Wherein:

23 L' is a neutral Lewis base; H is a hydrogen atom;

24 $[L'-H]$ is a Bronsted acid; M' is a metal or metalloid
 25 selected from the Groups subtended by Groups V-B to V-A of the
 26 Periodic Table of the Elements; i.e., Groups V-B, VI-B, VII-B,
 27 VIII-B, I-B, II-B, III-A, IV-A, and V-A;

28 Q_1 to Q_n are selected, independently, from the Group
 29 consisting of hydride radicals, dialkylamido radicals, alkoxide and
 30 aryloxy radicals, hydrocarbyl and substituted-hydro-carbyl radicals
 31 and organometalloid radicals and any one, but not more than one, of
 32 Q_1 to Q_n may be a halide radical - the remaining Q_1 to Q_n
 33 being, independently, selected from the foregoing radicals;

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1 m is an integer from 1 to 7; n is an integer from 2 to 8;
2 and $n - m = d$.

3

4 The preferred activator compounds comprising boron may be
5 represented by the following general formula:



7 Wherein:

8 L' is a neutral Lewis base; H is a hydrogen atom;

9 $[L'-H]^+$ is a Bronsted acid; B is boron in a valence state
10 of 3; Ar_1 and Ar_2 are the same or different aromatic or
11 substituted-aromatic hydrocarbon radicals containing from about 6 to
12 about 20 carbon atoms and may be linked to each other through a
13 stable bridging group; and X_3 and X_4 are radicals selected,
14 independently, from the group consisting of hydride radicals, halide
15 radicals, with the proviso that only X_3 or X_4 will be halide
16 at the same time, hydrocarbyl radicals containing from 1 to about 20
17 carbon atoms, substituted-hydrocarbyl radicals, wherein one or more
18 of the hydrogen atoms is replaced by a halogen atom, containing from
19 1 to about 20 carbon atoms, hydrocarbyl-substituted metal
20 (organometalloid) radicals wherein each hydrocarbyl substitution
21 contains from 1 to about 20 carbon atoms and said metal is selected
22 from Group IV-A of the Periodic Table of the Elements and the like.

23 In general, Ar_1 and Ar_2 may, independently, be any
24 aromatic or substituted-aromatic hydrocarbon radical containing from
25 about 6 to about 20 carbon atoms. Suitable aromatic radicals
26 include, but are not limited to, phenyl, naphthyl and anthracenyl
27 radicals. Suitable substituents include, but are not necessarily
28 limited to, hydrocarbyl radicals, organometalloid radicals, alkoxy
29 radicals, alkylamido radicals, fluoro and fluorohydrocarbyl radicals
30 and the like such as those useful as X_3 and X_4 . The
31 substituent may be ortho, meta or para, relative to the carbon atoms
32 bonded to the boron atom. When either or both X_3 and X_4 are

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1 a hydrocarbyl radical, each may be the same or a different aromatic
2 or substituted-aromatic radical as are Ar_1 and Ar_2 , or the
3 same may be a straight or branched alkyl, alkenyl or alkynyl radical
4 having from 1 to about 20 carbon atoms, a cyclic hydrocarbon radical
5 having from about 5 to about 8 carbon atoms or an alkyl-substituted
6 cyclic hydrocarbon radical having from about 6 to about 20 carbon
7 atoms. X_3 and X_4 may also, independently, be alkoxy or
8 dialkylamido radicals wherein the alkyl portion of said alkoxy and
9 dialkylamido radicals contain from 1 to about 20 carbon atoms,
10 hydrocarbyl radicals and organometalloid radicals having from 1 to
11 about 20 carbon atoms and the like. As indicated above, Ar_1 and
12 Ar_2 may be linked to each other. Similarly, either or both of
13 Ar_1 and Ar_2 could be linked to either X_3 or X_4 .
14 Finally, X_3 or X_4 may also be linked to each other through a
15 suitable bridging group.

16 Illustrative, but not limiting, examples of boron compounds
17 which may be used as an activator component in the preparation of the
18 improved catalysts of this invention are trialkyl-substituted
19 ammonium salts such as triethylammonium tetra(phenyl)boron,
20 tripropylammonium tetra(phenyl)boron, tri(n-butyl)ammonium
21 tetra(phenyl)boron, trimethylammonium tetra(p-tolyl)boron,
22 trimethylammonium tetra(o-tolyl)boron, tributylammonium
23 tetra(pentafluorophenyl)boron, tripropylammonium
24 tetra(o,p-dimethylphenyl)boron, tributylammonium
25 tetra(m,m-dimethylphenyl)boron, tributylammonium
26 tetra(p-tri-fluoromethylphenyl)boron, tributylammonium
27 tetra(pentafluorophenyl)boron, tri(n-butyl)ammonium
28 tetra(o-tolyl)boron and the like; N,N-dialkyl anilinium salts such as
29 N,N-dimethylanilinium tetra(phenyl)boron, N,N-diethylanilinium
30 tetra(phenyl)boron, N,N-2,4,6-pentamethylanilinium tetra(phenyl)boron
31 and the like; dialkyl ammonium salts such as di(i-propyl)ammonium
32 tetra(pentafluorophenyl)boron, dicyclohexylammonium
33 tetra(phenyl)boron and the like; and triaryl phosphonium salts such
34 as triphenylphosphonium tetra(phenyl)boron,
35 tri(methylphenyl)phosphonium tetra(phenyl)boron,

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1 tri(dimethylphenyl)phosphonium tetra(phenyl)boron and the like.
2 Suitable compounds containing other metals and metalloids
3 which are useful as activator components can be usefully employed.
4 In this regard, it should be noted that the foregoing list is not
5 intended to be exhaustive and that other useful boron compounds as
6 well as useful compounds containing other metals or metalloids would
7 be readily apparent to those skilled in the art from the foregoing
8 general equations.

The Catalyst Support

9 Typically, the support can be any of the known solid
10 catalyst supports, particularly porous supports, such as talc,
11 inorganic oxides, and resinous support materials such as
12 polyolefins. Preferably, the support material is an inorganic oxide
13 in particulate form.

14 Suitable inorganic oxide materials which are desirably
15 employed in accordance with this invention include Group II-A, III-A,
16 IV-A or IV-B metal oxides. The most preferred catalyst support
17 materials include silica, alumina, and silica-alumina and mixtures
18 thereof. Other inorganic oxides that may be employed either alone or
19 in combination with the silica, alumina or silica-alumina are
20 magnesia, titania, zirconia, and the like. Other suitable support
21 materials, however, can be employed, for example, finely divided
22 polyolefins such as finely divided polyethylene.

23 The metal oxides generally contain surface hydroxyl groups
24 which may react with and deactivate the ionic metallocene catalyst
25 when the catalyst is added to the slurried metal oxide support.
26 Therefore, it is preferred that the inorganic oxide support be
27 dehydrated prior to use, i.e. subjected to a thermal treatment in
28 order to remove water and reduce the concentration of the surface
29 hydroxyl groups. The treatment may be carried out in vacuum or while
30 purging with a dry inert gas such as nitrogen at a temperature of
31 about 100°C to about 1000°C, and preferably, from about 300°C to
32 about 800°C. Pressure considerations are not critical. The duration
33 of the thermal treatment can be from about 1 to about 24 hours.

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1 However, shorter or longer times can be employed.

2 As an alternative method of dehydration of the metal oxide
3 support material, chemical dehydration can be advantageously
4 employed. Chemical dehydration converts all water and hydroxyl
5 groups on the oxide surface to inert species. Useful chemical agents
6 are for example, chlorosilanes, such as trimethylchlorosilane, and
7 the like and alkyl aluminum reagents such as triethyl aluminum and
8 the like. The chemical dehydration is accomplished by slurring the
9 inorganic particulate material, such as, for example, silica in an
10 inert low boiling hydrocarbon, such as, for example, hexane. During
11 the chemical dehydration reaction, the silica should be maintained in
12 a moisture and oxygen-free atmosphere. To the silica slurry is then
13 added a low boiling inert hydrocarbon solution of the chemical
14 dehydrating agent.

15 The inorganic oxide support used in the preparation of the
16 catalyst may be any particulate oxide or mixed oxide as previously
17 described which has been thermally or chemically dehydrated such that
18 it is substantially free of adsorbed moisture.

19 The specific particle size, surface area and pore volume of
20 the inorganic oxide determine the amount of inorganic oxide that is
21 desirable to employ in preparing the catalyst compositions, as well
22 as affecting the properties of polymers formed with the aid of the
23 catalyst compositions. These properties must frequently be taken
24 into consideration in choosing an inorganic oxide for use in a
25 particular aspect of the invention. In general, optimum results are
26 usually obtained by the use of inorganic oxides having an average
27 particle size in the range of about 0.1 to 600 microns, preferably
28 about 0.3 to 80 microns; a surface area of about 50 to 1,000 square
29 meters per gram, preferably about 100 to 400 square meters per gram;
30 and a pore volume of about 0.5 to 3.5 cc per gram; preferably about
31 0.5 to 2 cc per gram.

Catalyst Preparation and Use

32 The supported ionic metallocene catalyst of this invention
33 may be prepared by combining the metallocene component, the activator

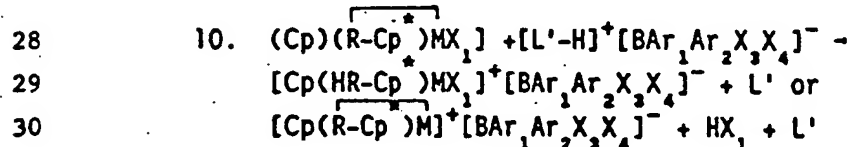
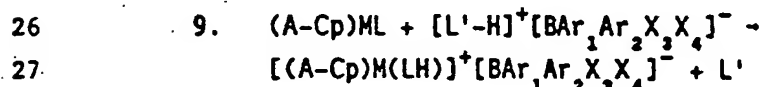
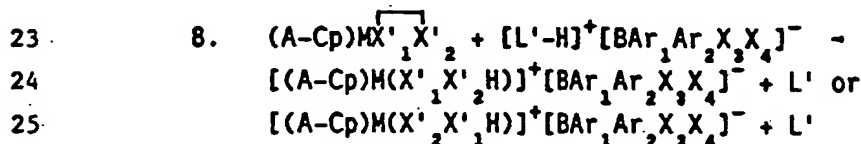
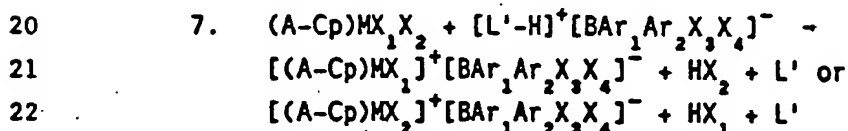
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- 1 component and the support in suitable solvents in one or more
2 steps.

A. Choice of Metallocene-Activator Pairs

3 In general, while most metallocene components identified
4 above may be combined with most activator components identified above
5 to produce an active olefin polymerization catalyst, it is desirable
6 for continuity of the polymerization operations that either the metal
7 cation initially formed from the metallocene component or a
8 decomposition product thereof be a relatively stable catalyst. It is
9 also desirable that the anion of the activator compound be stable to
10 hydrolysis when an ammonium salt is used. Further, it is desirable
11 that the acidity of the activator component be sufficient, relative
12 to the metallocene component to facilitate the needed proton
13 transfer. In general, bis(cyclopentadienyl) metal compounds which
14 can be hydrolyzed by aqueous solutions can be considered suitable as
15 metallocene components to form the catalysts described herein.

16 The chemical reactions which occur in forming the catalyst
17 of this invention may, when a preferred, boron-containing compound is
18 used as the second component, be represented by a reference to the
19 general formulae set forth herein as follows:



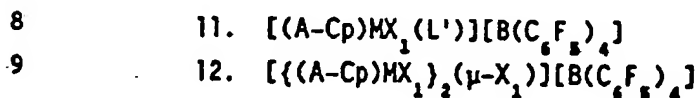
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1 In the foregoing reaction equations the symbols have been
2 previously defined. In general, the stability and rate of formation
3 of the products in the foregoing reaction equations, particularly the
4 metal cation, will vary depending upon the choice of the solvent, the
5 acidity of the $[L'-H]^+$ selected, the particular L' , the anion, the
6 temperature at which the reaction is completed and the particular
7 bis(cyclopentadienyl) derivative of the metal selected. Generally,
8 the initially formed ion-pair will be an active polymerization
9 catalyst and will polymerize α -olefins, diolefins, strained cyclic
10 olefins and acetylenically unsaturated monomers either alone or in
11 combination with other monomers. In some cases, however, the initial
12 metal cation will decompose to yield an active polymerization catalyst.

13 With respect to the combination of the metallocene component
14 with the activator component to form a catalyst of this invention, it
15 should be noted that the two compounds combined for preparation of the
16 active catalyst must be selected to avoid transfer of a fragment of
17 the anion, particularly an aryl group, to the metal cation, thereby
18 forming a catalytically inactive species. This can be done by steric
19 hindrance, resulting from substitutions on the cyclopentadienyl carbon
20 atoms as well as substitutions on the aromatic carbon atoms of the
21 anion. It follows, then, that the metallocene components comprising
22 perhydrocarbyl-substituted cyclopentadienyl radicals could be
23 effectively used with a broader range of activator compounds than
24 could metallocene components comprising unsubstituted cyclopentadienyl
25 radicals. As the amount and size of the substitutions on the
26 cyclopentadienyl radicals are reduced however, more effective
27 catalysts are obtained with activator compounds containing anions
28 which are more resistant to degradation, such as those with
29 substituents on the ortho positions of the phenyl rings. Another
30 means of rendering the anion more resistant to degradation is afforded
31 by fluorine substitution, especially perfluoro-substitution, in the
32 anion. Fluoro-substituted stabilizing anions may, then, be used with
33 a broader range of metal compound (first components). Activators in
34 which the anions comprise pentafluorophenyl groups are preferred for
35 preparing ion-pair metallocene catalysts of this invention.

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1 It is preferred that the mole ratio of metallocene component
 2 to activator component be 1:1 or greater. In a reaction corresponding
 3 to general formula 1, when the anion comprises pentafluorophenyl
 4 groups, two structurally distinct forms of thermally stable ionic
 5 catalysts have been identified by NMR spectroscopy and are shown in
 6 general formulae 5 and 6, using tetrakis(pentafluorophenyl)boron as a
 7 representative anion:



10 In the foregoing formulae, the symbols A-Cp, M, L', and X_1
 11 correspond to the definitions set forth in general formulae 1-4. The
 12 symbol "Y" indicates the ligand X^1 bridges the two metal
 13 centers. In both general formulae 5 and 6, NMR experiments indicate
 14 that the fluorinated boron anion is completely non-coordinating.
 15 When the molar ratio of metallocene component to activator component
 16 is 1:1, L' weakly coordinates to and stabilizes the metallocene cation
 17 when L' is an aniline derivative, for example N,N-dimethylaniline, to
 18 give an ionic catalyst of general formula 5. When the molar ratio of
 19 metallocene component to activator component is greater than 1:1 an X
 20 group, for examples, a methyl group of an excess
 21 $(A-Cp)M(CH_3)_2$ molecule when $(A-Cp)M(CH_3)_2$ is the
 22 metallocene used, weakly coordinates to and stabilizes the
 23 metallocene cation to give an ionic catalyst of general formula 6.

B. Catalyst Preparation

24 The supported catalyst of this invention can be prepared by
 25 combining the metallocene, activator components and support in one or
 26 more suitable solvents or diluent. Suitable solvents and/or diluents
 27 include, but are not necessarily limited to, straight and
 28 branched-chain hydrocarbons such as isobutane, butane, pentane,
 29 hexane, heptane, octane and the like; cyclic and
 30 alicyclic hydrocarbons such as cyclohexane, cycloheptane,
 31 methylcyclohexane, methylcycloheptane and the like; and aromatic and

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1 alkyl-substituted aromatic compounds such as benzene, toluene, xylene
2 and the like.

3 It is preferred that the catalyst components be handled in an
4 inert, moisture-free, oxygen-free environment such as argon, nitrogen
5 or helium because of the sensitivity of the catalyst components to
6 moisture and oxygen.

7 In a preferred method, the metallocene and activator
8 components are combined in a first step in an aromatic solvent to
9 produce a solution the reaction product. This reaction may be carried
10 out in the temperature range -100° to about 300°C, preferably about 0°
11 to about 100°C. Holding times to allow for the completion of the
12 reaction may range from about 10 seconds to about 60 minutes depending
13 upon variables such as reaction temperature and choice of reactants.

14 The solution produced by combining the metallocene and
15 activator components is then contacted with the support. The method
16 of contact may vary, but it is preferred that the solution be added to
17 a rapidly stirred slurry of the catalyst support in a hydrocarbon
18 solvent, preferably an aliphatic solvent and especially pentane.

19 In another preferred method, in a first step, the activator
20 component is dissolved in an aromatic solvent with the support to
21 produce a supported activator component. This reaction is carried out
22 at a temperature sufficient to produce a homogeneous solution of the
23 activator component, preferably between about 25°C to about 200°C.
24 The aromatic solvent is then removed to leave a free-flowing supported
25 material. The supported material is then contacted with the
26 metallocene component, preferably in an aliphatic solvent to produce
27 the supported catalyst.

28 Regardless of the method, the active supported catalyst can
29 be recovered by evaporation of the solvent to obtain a free-flowing
30 solid or alternatively, the active supported catalyst can be
31 maintained in its slurry state for direct use.

32 Contact temperatures may range from about 0° to about 100°C
33 depending upon the solvents used. Contact times may vary from about
34 10 seconds to about 60 minutes, longer contact times than 60 minutes
35 not providing any significant additional benefits.

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1 In the preparation of the supported catalyst, the reagents
2 should be combined to provide a catalyst concentration (metallocene
3 and activator) on the support of from about 0.01 wt % to about 20 wt
4 %, preferably about 1 wt % to about 5 wt % based upon the weight of
5 the support.

6 In a most preferred embodiment of the present invention,
7 bis(cyclopentadienyl)zirconium dimethyl or
8 bis(cyclopentadienyl)hafnium dimethyl will be reacted with
9 N,N-dimethylanilinium tetra(pentafluorophenyl)boron and then contacted
10 with an alumina, silica or silica-alumina support to produce the most
11 preferred catalyst of the present invention. The metallocene and
12 activator components will be combined at a temperature within the
13 range -100° to about 300°C, preferably from about 0°C to about 100°C,
14 and preferably in an aromatic hydrocarbon solvent, most preferably
15 toluene. A nominal holding time within the range from about 10
16 seconds to about 60 minutes will be sufficient before the mixture is
17 contacted with a slurry of the dried support material in an aliphatic
18 solvent for a contacting period of from about 10 seconds to about 60
19 minutes.

20 In another preferred method, in a first step,
21 N,N-dimethylanilinium tetra(pentafluorophenyl)boron is dissolved in an
22 aromatic solvent maintained at a temperature sufficient to dissolve
23 the activator component. The support is slurried therein and the
24 activator and support are reacted for about 1 minute to about 1 hour
25 to produce a supported activator component. The aromatic solvent is
26 removed to leave a free-flowing support material containing the
27 activator component. This supported activator component is then
28 contacted with bis(cyclopentadienyl)zirconium dimethyl or
29 bis(cyclopentadienyl)hafnium dimethyl, preferably in an aliphatic
30 solvent to produce the supported catalyst.

31 With either method, the active supported catalyst can be
32 recovered by evaporation of the solvent to obtain a free-flowing solid
33 or, alternately, the active supported catalyst can be maintained in a
34 slurry state for direct use.

C. Catalyst Use

35 The supported ionic metallocene catalyst may be used to

1 polymerize α -olefins and acetylenically unsaturated monomers having
2 from 2 to about 18 carbon atoms and/or diolefins having from 4 to
3 about 18 carbon atoms either alone or in combination. The catalyst
4 may also be used to polymerize α -olefins, diolefins, strained cyclic
5 olefins and/or acetylenically unsaturated monomers in combination with
6 other unsaturated monomers. While the catalyst is active for this
7 broad range of olefinic monomer feedstock, α -olefin polymerization
8 is preferred especially the homopolymerization of ethylene or the
9 copolymerization of ethylene with olefins having from 3 to 10 carbon
10 atoms.

11 In a preferred embodiment of the present invention, the
12 metallocene component will be a bis(cyclopentadienyl)-Group IV-B metal
13 compound containing two, independently, substituted or unsubstituted
14 cyclopentadienyl radicals and one or two lower alkyl substituents
15 and/or one or two hydride substituents and the activator component
16 will be a tri-substituted ammonium salt of a fluorinated tetraphenyl
17 boron anion. Each of the tri-substitutions in the ammonium cation
18 will be the same or a different lower alkyl or aryl radical. By lower
19 alkyl is meant an alkyl radical containing from 1 to 4 carbon atoms.
20 N,N-dimethylanilinium tetra(pentafluorophenyl)boron is particularly
21 preferred. Alumina, silica or silica-alumina will be the preferred
22 support for producing the supported ionic metallocene catalyst.

23 Certain of the catalysts of this invention, particularly
24 those based on hafnocenes - using the catalyst produced from the
25 reaction of bis(cyclopentadienyl)hafnium dimethyl and the
26 tri-substituted ammonium salt of tetra(pentafluorophenyl)boron as an
27 example - when used as described herein for the polymerization and
28 copolymerization of α -olefins, diolefins, and/or acetylenically
29 unsaturated monomers, in the absence of a chain transfer agent, can
30 lead to the production of extremely high molecular weight polymers and
31 copolymers having relatively narrow molecular weight distributions.
32 In this regard, it should be noted that homopolymers and copolymers
33 having molecular weights up to about 2×10^6 or higher and
34 molecular weight distributions within the range of about 1.5 to about
35 3 or greater can be produced with the catalysts of this invention.

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1 Combinations of two or more ionic metallocene catalyst with the
2 support can be employed in order to obtain broader MWD such as up to
3 about 15 or greater. Alternatively, two or more separately supported
4 catalysts can be used to obtain broad MWD polymers and copolymers.

5 Supported catalysts of this invention containing a
6 metallocene component which is either a pure enantiomer or the racemic
7 mixture of two enantiomers of a rigid, chiral metallocene can
8 polymerize prochiral olefins (propylene and higher α -olefins) to
9 crystalline polymers including syndiotactic and isotactic polymers.
10 Bis(cyclopentadienyl)metal compounds in which each of the
11 cyclopentadienyl radicals is substituted and containing a covalent
12 bridging group between the two cyclopentadienyl radicals are
13 particularly useful for isotactic polymerizations of this type.
14 Prochiral metallocenes, for example those based on complexes of
15 propyl-2-cyclopentadienyl-2-(1-fluorenyl) hafnium, can be used to
16 polymerize propylene or higher α -olefins to syndiotactic polymers.

17 The supported catalysts may be most usefully employed in gas
18 or slurry phase processes, both of which are known to those of skill
19 in the art. Thus, polymerizations using the invention supported
20 catalysts may be conducted by either of these processes, generally at
21 a temperature in the range of about 0°-160°C or even higher, and under
22 atmospheric, subatmospheric, or superatmospheric pressure conditions.

23 A slurry polymerization process can utilize sub- or
24 super-atmospheric pressures and temperatures in the range of
25 -80-250°C. In a slurry polymerization, a suspension of solid,
26 particulate polymer is formed in a liquid polymerization medium to
27 which ethylene, α -olefin, diolefin, cyclic olefin or acetylenically
28 unsaturated comonomer, hydrogen and catalyst are added. Alkanes and
29 cycloalkanes, such as butane, pentane, hexane, or cyclohexane, are
30 preferred with C₄ to C₁₀ alkanes especially preferred.
31 Preferred solvents also include liquid olefins which may act as
32 monomers or comonomers including ethylene, propylene, butadiene,
33 cyclopentene, 1-hexene, 3-methyl-1-pentene, 4-methyl-1-pentene,
34 1,4-hexadiene, 1-octene, 1-decene and the like.

35 A gas-phase polymerization process utilizes superatmospheric

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1 pressure and temperatures in the range of about 50° - 120°C.
2 Gas-phase polymerization can be performed in a stirred or fluidized
3 bed of catalyst and product particles in a pressure vessel adapted to
4 permit the separation of product particles from unreacted gases.
5 Thermostated ethylene, comonomer, hydrogen and an inert diluent gas
6 such as nitrogen can be introduced or recirculated so as to maintain
7 the particles at a temperature of 50° - 120°C. Polymer product can be
8 withdrawn continuously or semi-continuously at a rate such as to
9 maintain a constant product inventory in the reactor. After
10 polymerization and deactivation of the catalyst, the product polymer
11 can be recovered by any suitable means. In commercial practice, the
12 polymer product can be recovered directly from the gas phase reactor,
13 freed of residual monomer with a nitrogen purge, and used without
14 further deactivation or catalyst removal. The polymer obtained can be
15 extruded into water and cut into pellets or other suitable comminuted
16 shapes. Pigments, antioxidants and other additives, as is known in
17 the art, may be added to the polymer.

18 While it is a characteristic of the invention supported
19 catalyst that the produced polymers have a narrow molecular weight
20 distribution, broad molecular weight distribution polymers may be
21 produced by using two or more metallocenes or two or more activators.

22 The advantages of the instant invention will be more readily
23 appreciated by reference to the following illustrative, non-limiting
24 examples.

Example 1

25 A supported catalyst was prepared by reacting
26 bis(cyclopentadienyl)hafnium dimethyl (30 mg) with
27 N,N-dimethylanilinium tetrakis(pentafluorophenyl)boron (60 mg) in
28 toluene (8 ml). This solution was added slowly to a suspension of
29 basic alumina (Brockman Activity I, dried overnight at 100°C under
30 vacuum; 2.0 g) in pentane (25 ml). The mixture was allowed to stir
31 for about 3 minutes at room temperature. The supernatant solution was
32 then decanted from the solid material and the solids reslurried with
33 fresh pentane. The supernatant solution was again decanted from the

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1 solids and the solids suspended in fresh pentane (ca. 30 ml). This
2 suspension was transferred, under nitrogen, by means of a double-ended
3 needle into a 1 liter stainless-steel autoclave containing 400 ml of
4 dry, deoxygenated hexane and which had been previously flushed with
5 nitrogen. The autoclave was then pressured to 90 psig with ethylene
6 and stirred at 40°C. After 30 minutes, the autoclave was cooled,
7 vented and the contents separated by filtration. The yield of linear
8 granular, free-flowing polyethylene was 11.2 g. The polymer had a
9 weight-average molecular weight of 594,000 and a molecular weight
10 distribution of 2.15.

Example 2

11 The supported catalyst of Example 1 was used to polymerize
12 ethylene in a process similar to that of Example 1 except that the
13 autoclave was pressured to 300 psig of ethylene. The yield of linear
14 granular, free-flowing polyethylene was 48.5 g with a bulk density of
15 0.17 g/cc versus 0.07 g/cc when an unsupported, homogeneous catalyst
16 is used.

Example 3

17 A supported catalyst was prepared by reacting
18 bis(cyclopentadienyl)zirconium dimethyl (20 mg) with
19 N,N-dimethylanilinium tetrakis(pentafluorophenyl)boron (60 mg) in
20 toluene (20 ml). This solution was added slowly to a suspension of
21 basic alumina (2.0 g) in pentane (25 ml). The mixture was allowed to
22 stir for about 3 minutes at room temperature. The supernatant
23 solution was decanted from the solid material and the solids
24 reslurried with fresh pentane. The supernatant solution was again
25 decanted from the solids and the solids were suspended in fresh
26 pentane (ca. 30 ml). This suspension was transferred, under nitrogen,
27 by means of a double-ended needle into a 1 liter stainless-steel
28 autoclave, previously flushed with nitrogen, containing 400 ml of dry,
29 deoxygenated hexane. The autoclave was then pressured to 400 psig
30 with ethylene and stirred at 40°C. After 30 minutes, the autoclave
31 was cooled and vented and the contents isolated by filtration. The

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- 1 yield of linear granular, free-flowing polyethylene was 4.7 g with a
2 weight-average molecular weight of 515,000 and a MWD of 1.74.

Example 4

- 4 A supported catalyst was prepared as in Example 1 except that
5 2.0 g of Davison 948 silica (dried at 800°C with a nitrogen purge) was
6 used in place of alumina. The catalyst was used to polymerize
7 ethylene in a process similar to that of Example 2. The yield of
8 linear granular, free-flowing polyethylene was 11.1 g with a
9 weight-average molecular weight of 1,384,000 and a MWD of 1.67.

Example 5

- 10 A supported catalyst was prepared as in Example 4 except that
11 20 mg of bis(cyclopentadienyl)zirconium dimethyl was used in place of
12 bis(cyclopentadienyl)hafnium dimethyl. This catalyst was used to
13 polymerize ethylene in a process similar to that of Example 2. The
14 yield of linear granular, free-flowing polyethylene formed was 2.7 g
15 with a weight-average molecular weight of 759,000 and a MWD of 1.67.

Example 6

- 16 A supported catalyst was prepared by reacting
17 bis(cyclopentadienyl)hafnium dimethyl (45 mg) with
18 N,N-dimethylanilinium tetrakis(pentafluorophenyl)boron (90 mg) in
19 toluene (20 ml). This solution was added slowly to a suspension of
20 basic alumina (3.0 g) in pentane (25 ml). The mixture was allowed to
21 stir for about 3 minutes at room temperature. The solution was
22 decanted from the solid material and the solids reslurried with fresh
23 pentane. The supernatant solution was again decanted from the solids
24 and the solids were dried in an atmosphere of nitrogen. This
25 suspension was injected into a 1 liter stainless-steel autoclave,
26 previously flushed with nitrogen, containing 300 ml of propylene, by
27 washing 50 ml of propylene through a stainless-steel catalyst addition
28 tube containing the solid catalyst. The autoclave was then pressured
29 to 100 psig with ethylene and stirred at 50°C. After 15 minutes, the
30 autoclave was cooled and vented and the polymer product was isolated.

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1 The yield of granular ethylene-propylene copolymer was 38 g. This
2 polymer, which contained 21 wt. % ethylene, had a weight-average
3 molecular weight of 423,000 and a molecular weight distribution of
4 2.88.

Example 7

5 Ethylene and propylene was copolymerized in a manner similar
6 to Example 6, with the exceptions that the ethylene pressure was
7 increased to 200 psig and the autoclave was heated to 45°C. The yield
8 of granular ethylene-propylene copolymer was 57.1 g. This polymer,
9 which contained 52 wt. % ethylene, had a weight-average molecular
10 weight of 1,006,000 and a molecular weight distribution of 2.01.

Example 8

11 A supported catalyst of this invention was prepared by
12 reacting rac-dimethylsilylbis(indenyl)hafnium dimethyl (29 mg) with
13 N,N-dimethylanilinium tetrakis(pentafluorophenyl)boron (45 mg) in
14 toluene (10 ml). This solution was added slowly to a suspension of
15 basic alumina (1.5 g) in pentane (25 ml). The mixture was allowed to
16 stir for about 3 minutes at room temperature. The supernatant
17 solution was decanted from the solid material and the solids
18 reslurried with fresh pentane. The supernatant solution was again
19 decanted from the solids and the solids were suspended in fresh
20 pentane (ca. 30 ml). This suspension was transferred under nitrogen,
21 by means of double-ended needle into a 1 liter stainless-steel
22 autoclave, previously flushed with nitrogen, containing 400 ml of dry,
23 deoxygenated hexane. Propylene (200 ml) was added to the autoclave,
24 which was stirred at 50°C. After 1.75 hours, the autoclave was cooled
25 and vented and the contents separated by filtration. The yield of
26 isotactic polypropylene was 9.5 g. This polymer had a melting point
27 of 127°C, as determined by differential scanning calorimetry, a weight
28 average molecular weight of 181,000 and a molecular weight
29 distribution of 1.95. Analysis by C-13 NMR spectroscopy indicated
30 that the polypropylene was 92% isotactic.

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Example 9

1 A 1 liter stainless-steel autoclave was charged with virgin
2 polypropylene (14 mesh, 190 g) and heated to 85°C under a dynamic
3 nitrogen purge. After cooling to 50°C, the catalyst of Example 1 (2.0
4 g) was added to the reactor from a stainless-steel catalyst addition
5 tube using high-pressure nitrogen. After venting off the excess
6 nitrogen pressure, ethylene was admitted to the stirred polymer bed to
7 maintain a constant flow. The pressure inside the autoclave ranged
8 from 10 to 35 psig. The maximum temperature in the autoclave reached
9 70°C. After 1 hour, the autoclave was cooled and vented and the
10 polymer mixture isolated. The net increase in the polymer weight was
11 38 g. A portion of the polyethylene was sieved from the polypropylene
12 stirring aid and was found to have a weight-average molecular weight
13 of 175,000 and a MWD of 2.53.

Example 10

14 Alumina (1.0 g), slurried in 10 ml of pentane, was treated
15 for 15 minutes with 1 ml of a 1 M solution of triethylaluminum in
16 hexane. The support was separated from the liquid by decantation,
17 washed twice with 10 ml of pentane and dried in vacuo.

18 N,N-dimethylanilinium tetrakis (pentafluorophenyl)boron (30
19 mg) was heated in toluene (25 ml) to produce a homogeneous solution.
20 The warm solution was added dropwise to the support prepared as
21 described above. The solvent was removed in vacuo to leave a
22 free-flowing supported material.

23 This support material (1.0 g) was slurried in 10 ml of
24 pentane. To this was added dropwise 5 ml of a pentane solution
25 containing bis(cyclopentadienyl) hafnium dimethyl (15 mg). After
26 stirring at room temperature for 15 minutes, the solvent was removed
27 in vacuo to leave a free-flowing supported catalyst.

Example 11

28 500 mg. of the supported catalyst of Example 10 was used to
29 polymerize ethylene in a process similar to Example 1 except that the
30 autoclave was pressured to 400 psig with ethylene and was heated to

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1 80°C. The yield of linear granular, free-flowing polyethylene was 132
2 g.

3 Although the invention has been described with reference to
4 its preferred embodiments, those of ordinary skill in the art may,
5 upon reading this disclosure, appreciate changes and modifications
6 which do not depart from the scope and spirit of the invention as
7 described above or claimed hereafter.

Example 12

8 Davison 952 silica (1 g) was slurried in pentane
9 and treated with 1 ml of a 1 M solution of triethylaluminum
10 in hexane. The support was separated from the liquid by
11 decantation, washed twice with pentane and dried in vacuo.

12 N,N-dimethylanilinium tetrakis
13 (pentafluorophenyl)boron (30 mg) was heated in toluene to
14 produce a homogeneous solution. The warm solution was added
15 dropwise to the support prepared as described above. The
16 solvent was removed in vacuo to leave a free-flowing
17 supported material.

18 This support material was slurried in 10 ml of
19 pentane. To this was added dropwise 10 ml of a pentane
20 solution containing 15 mg of rac-
21 dimethylsilylbis(tetrahydroindenyl) - zirconium dimethyl.
22 After stirring at room temperature for 15 minutes, the
23 solvent was removed in vacuo to leave a free-flowing
24 supported catalyst.

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Example 13

1 The catalyst of Example 12 (887 mg) was injected
2 by means of high-pressure nitrogen into a 1 liter stainless-
3 steel autoclave, which was previously flushed with nitrogen,
4 containing 300 ml dry, deoxygenated propylene at 40 degrees
5 C. After 20 minutes, the contents isolated the yield of
6 isotactic polypropylene was 101.7 g.

Example 14

7 Davison 948 silica (3 g), dehydrated at 800
8 degrees with an nitrogen purge was slurried in pentane and
9 treated with 8 ml of a 1.5 M solution of triethylaluminum in
10 hexane. The support was separated from the liquid by
11 decantation, washed six times with pentane, and dried in
12 vacuo.

13 N,N-dimethylanilinium
14 tetrakis(pentafluorophenyl)baron (96 mg) was heated in 30 ml
15 warm toluene, to produce a homogeneous solution. The warm
16 solution was added dropwise to a toluene slurry of the
17 support prepared as described above. The solvent was
18 removed in vacuo with gentle heating to leave a free-flowing
19 supported material.

20 This supported material was reslurried in pentane.
21 To this was added dropwise 20 ml of a pentane solution
22 containing 48 mg of bis(cyclopentadienyl)hafnium dimethyl.
23 After stirring at room temperature for 15 minutes, the
24 solvent was removed in vacuo to leave a free-flowing
25 supported catalyst.

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Example 15

1 The catalyst of Example 14 (100 mg) was injected
2 with 100 ml hexane into a 1 liter stainless-steel autoclave,
3 which was previously flushed with nitrogen, containing 300
4 ml of dry, deoxygenated hexane and pressurized with 200 psi
5 ethylene at 60 degrees C. After 20 minutes the autoclave
6 was cooled and vented and the contents isolated by
7 filtration. The yield of linear polyethylene was 78.7 g.

CLAIMS:

1. A method for preparing a supported ionic catalyst comprising the steps of:

(a) combining, in a solvent or diluent

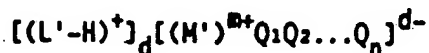
(i) at least one metallocene component comprising a bis(cyclopentadienyl)metal compound containing at least one ligand capable of reacting with a proton, said metal being selected from the group consisting of titanium, zirconium and hafnium,

(ii) at least one activator component comprising a cation capable of donating a proton and an anion, said anion being a single coordination complex comprising a plurality of lipophilic radicals covalently coordinated to and shielding a central charge-bearing metal or metalloid atom, said anion being bulky, labile and capable of stabilizing the metal cation formed as a result of reaction between the two, and

(iii) a catalyst support material suspended in a suitable solvent; and

(b) recovering a supported catalyst product as a free-flowing solid or slurry.

2. The method of claim 1 wherein said activator component is represented by the following general formula:



wherein:

L' is a neutral Lewis base; H is a hydrogen atom;

[L'-H]⁺ is a Bronsted acid;

M' is a metal or metalloid selected from the groups subtended by Groups V-B to V-A of the Periodic Table of the Elements; i.e., Groups V-B, VI-B, VII-B, VIII, I-B, II-B, III-A, IV-A and V-A;

Q₁ to Q_n are selected, independently, from the group consisting of hydride radicals, dialkylamido radicals, alkoxide and

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aryloxy radicals, hydrocarbyl and substituted-hydrocarbyl radicals and organometalloid radicals and any one, but not more than one, of Q_1 to Q_n may be a halide radical with the remaining Q_1 to Q_n being, independently, selected from the foregoing radicals;

m is an integer from 1 to 7; n is an integer from 2 to 8; and $n - m = d$.

3. The method of claim 2 wherein said activator component is represented by the following general formula:

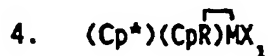
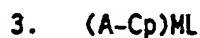
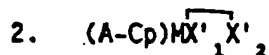
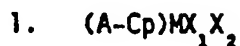


wherein:

L' is a neutral Lewis base; H is a hydrogen atom;
 $[L'-H]^+$ is a Bronsted acid; B is boron in a valence state of 3;

Ar_1 and Ar_2 are the same or different aromatic or substituted-aromatic hydrocarbon radicals, said radicals being optionally linked to each other through a stable bridging group; and X_3 and X_4 are, independently, selected from the group consisting of hydride radicals, halide radicals, hydrocarbyl and substituted-hydrocarbyl radicals and organometalloid radicals.

4. The method of claim 3 wherein said bis(cyclopentadienyl)metal compound is represented by one of the following general formulae:



Wherein:

M is a metal selected from the group consisting of titanium, zirconium and hafnium;

(A-Cp) comprises (Cp)(Cp*) or Cp-A'-Cp* and Cp and Cp* are the same or different substituted or unsubstituted cyclopentadienyl radicals;

A' is a covalent bridging group; L is an olefin, diolefin or aryne ligand;

X₁ and X₂ are, independently, selected from the group consisting of hydride radicals, hydrocarbyl radicals, substituted-hydrocarbyl radicals and organometalloid radicals;

X'₁ and X'₂ are joined and bound to the metal atom to form a metallacycle, in which the metal atom, X'₁ and X'₂ form a hydrocarbocyclic ring containing from about 3 to about 20 carbon atoms; and

R is a substituent on one of the cyclopentadienyl radicals which is also bound to the metal atom.

5. The method of claim 1 wherein said support is selected from alumina, silica, alumina-silica, talc, magnesia, zirconia, titania, finely divided polyolefins or mixtures thereof.

6. The method of claim 5 wherein said support is alumina, silica or mixtures thereof.

7. The method of claim 4 wherein the metallocene is bis(cyclopentadienyl)zirconium dimethyl or bis(cyclopentadienyl)hafnium dimethyl; the activator is N,N-dimethylanilinium tetrakis(pentafluorophenyl)boron; and the support is alumina or silica.

8. The method in of claim 1, wherein the at least one metallocene and the at least one activator component are reacted in a solvent or diluent and the direct product or the decomposition product of said direct product is contacted in a suitable solvent with a

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catalyst support material and thereafter the supported catalyst product is recovered as a free-flowing solid or slurry.

9. The method of claim 1, wherein the activator component is dissolved in an aromatic solvent and the support is slurried therein and allowed to react, the supported activator component is then contacted with the metallocene component in an aliphatic method.

10. A catalyst comprising the supported ionic catalyst obtained by the method of claim 1.

INTERNATIONAL SEARCH REPORT

International Application No. PCT/US 90/07669

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶ According to International Patent Classification (IPC) or to both National Classification and IPC IPC ⁵ : C 08 F 4/76, 4/603, 10/00																	
II. FIELDS SEARCHED <div style="text-align: right; font-size: small;">Minimum Documentation Searched ⁷</div> <table style="width: 100%; border: none;"> <tr> <td style="width: 30%; border: none;">Classification System</td> <td style="border: none;">Classification Symbols</td> </tr> <tr> <td style="border: none; padding: 10px;">IPC⁵</td> <td style="border: none; padding: 10px;">C 08 F</td> </tr> </table> <div style="text-align: center; font-size: x-small; margin-top: 10px;"> Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸ </div>			Classification System	Classification Symbols	IPC ⁵	C 08 F											
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III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹ <table border="1" style="width: 100%; border-collapse: collapse; font-size: x-small;"> <thead> <tr> <th style="width: 10%;">Category ¹⁰</th> <th style="width: 70%;">Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²</th> <th style="width: 20%;">Relevant to Claim No. ¹³</th> </tr> </thead> <tbody> <tr> <td style="text-align: center; vertical-align: top;">A</td> <td>EP, A, 0277004 (EXXON) 3 August 1988 see the claims cited in the application ---</td> <td style="text-align: center; vertical-align: top;">1</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">A</td> <td>EP, A, 0232595 (EXXON) 19 August 1987 see the claims cited in the application ---</td> <td style="text-align: center; vertical-align: top;">1</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">A</td> <td>EP, A, 0277003 (EXXON) 3 August 1988 see the claims ---</td> <td style="text-align: center; vertical-align: top;">1</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">A</td> <td>US, A, 4017525 (R.A. SETTERQUIST) 12 April 1977 see the claims -----</td> <td style="text-align: center; vertical-align: top;">1</td> </tr> </tbody> </table>			Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³	A	EP, A, 0277004 (EXXON) 3 August 1988 see the claims cited in the application ---	1	A	EP, A, 0232595 (EXXON) 19 August 1987 see the claims cited in the application ---	1	A	EP, A, 0277003 (EXXON) 3 August 1988 see the claims ---	1	A	US, A, 4017525 (R.A. SETTERQUIST) 12 April 1977 see the claims -----	1
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A	US, A, 4017525 (R.A. SETTERQUIST) 12 April 1977 see the claims -----	1															
<div style="font-size: x-small;"> ¹⁰ Special categories of cited documents: <ul style="list-style-type: none"> "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed </div>		<div style="font-size: x-small;"> ¹¹ "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention ¹² "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step ¹³ "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. ¹⁴ "G" document member of the same patent family </div>															
IV. CERTIFICATION <table style="width: 100%; border: none;"> <tr> <td style="width: 50%; border: none; vertical-align: top;"> <div style="font-size: x-small;">Date of the Actual Completion of the International Search</div> <div style="text-align: center; padding: 10px;">18th April 1991</div> <div style="font-size: x-small;">International Searching Authority</div> <div style="text-align: center; padding: 5px;">EUROPEAN PATENT OFFICE</div> </td> <td style="width: 50%; border: none; vertical-align: top;"> <div style="font-size: x-small;">Date of Mailing of this International Search Report</div> <div style="text-align: center; padding: 10px;">13. 06. 91</div> <div style="font-size: x-small;">Signature of Authorized Officer</div> <div style="text-align: center; padding: 5px;">miss T. MORTENSEN </div> </td> </tr> </table>			<div style="font-size: x-small;">Date of the Actual Completion of the International Search</div> <div style="text-align: center; padding: 10px;">18th April 1991</div> <div style="font-size: x-small;">International Searching Authority</div> <div style="text-align: center; padding: 5px;">EUROPEAN PATENT OFFICE</div>	<div style="font-size: x-small;">Date of Mailing of this International Search Report</div> <div style="text-align: center; padding: 10px;">13. 06. 91</div> <div style="font-size: x-small;">Signature of Authorized Officer</div> <div style="text-align: center; padding: 5px;">miss T. MORTENSEN </div>													
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**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

US 9007669
SA 44096

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 04/06/91. The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A- 0277004	03-08-88	AU-A- 1245288	24-08-88
		JP-T- 1502036	13-07-89
		WO-A- 8805793	11-08-88
EP-A- 0232595	19-08-87	US-A- 4701432	20-10-87
		AU-B- 599622	26-07-90
		AU-A- 6728587	02-06-87
		EP-A- 0245482	19-11-87
		JP-T- 63501369	26-05-88
		WO-A- 8702991	21-05-87
EP-A- 0277003	03-08-88	AU-A- 1294588	24-08-88
		JP-T- 1501950	06-07-89
		WO-A- 8805792	11-08-88
US-A- 4017525	12-04-77	None	